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## **Effects of Selected Ligands on U(VI) Immobilization by Zerovalent Iron**

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### **Abstract**

The effects of  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ , EDTA,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ , and humic substances (HS) on U(VI) co-precipitation from aqueous solutions by zerovalent iron (ZVI) in the neutral pH range was investigated. Not shaken batch experiments were conducted for 14 days mostly with 15 g/L of five different ZVI materials and 10 mM of selected ligands and 20 mg/l (0.084 mM) of an U(VI) solution. Apart from  $\text{Cl}^-$  all tested ligands induced a decrease of U(VI) co-precipitation. This decrease is attributed to surface adsorption and complexation of the ligands to reactive sites on the surface of ZVI and their corrosion products. The extent of U(VI) removal decrease was not uniform for the five materials. Generally, groundwater with elevated EDTA concentration should not be remediated with the ZVI barrier technology. A rational selection of material can enable the selection of appropriated materials for any specific site with other tested ligands. The response of the system on pre-treating two ZVI materials with 250 mM HCl indicated that in situ generated corrosion products favor irreversible U(VI) uptake. Thus for the long term performance of ZVI barrier, iron dissolution should continue such that fresh iron oxide is always available for U(VI) co-precipitation.

**Key Words:** ligand, in-situ remediation, uranium, zerovalent iron.

## Introduction

Uranium (U) contamination of groundwater is widespread in former mining areas. In some areas, contaminated groundwaters have U contents up to 50 mg/L.<sup>1,2</sup> The US EPA maximum contaminant level for U is 30 µg/L. Therefore efficient and affordable techniques are necessary to mitigate the health risk by reducing U removal from the mine waters and contaminated ground waters. Zerovalent iron (ZVI) has been discussed in the literature as a U removing reagent in permeable reactive walls.

The primary goal of using ZVI materials in mitigating U in groundwater was to use Fe<sup>0</sup> as an electron donor to chemically reduce aqueous mobile U(VI) species to less soluble U(IV) precipitates.<sup>2-5</sup> Recently, it was demonstrated that under the experimental conditions of the cited authors, U(VI) is rather almost irreversible entrapped in the matrix of in situ generated and aged corrosion products: co-precipitation.<sup>6-8</sup> This observation is confirmed by field speciation data showing that at least 50 % of removed uranium remained in the oxidation state VI.<sup>9</sup> Therefore, the long term stability of fixed U(VI) has to be reconsidered.<sup>10</sup> Moreover, it is important to thoroughly understand the effects of geochemical variables such as chemical composition of the plume, pH, and redox potential on the behavior of the PRB (ref. 11 and references therein). It is expected that major ions, organic and inorganic ligands, will affect U(VI) co-precipitation through chemical interactions both with Fe<sup>0</sup> and its corrosion products (iron oxides and green rusts) in a PRB system, which may influence the effectiveness and longevity of PRB for contaminant removal.

From the uranium geochemistry and the corrosion properties of iron, four classes of groundwater constituents can be distinguished:

1. the first class is that of electro-active water constituents, that favor iron corrosion because of higher value of their standard electrode potential (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>...);
2. the second class is that of components that readily form complexes with U(VI) ions (humic substances - HS; CO<sub>3</sub><sup>2-</sup>; PO<sub>4</sub><sup>3-</sup>),

3. the third class is that of other electro-active contaminants, that will compete with U(VI) for removal by means of ZVI ( $\text{CrO}_4^{2-}$ ,  $\text{Pb}^{2+}$ ,  $\text{TcO}_4^-$ , ...);

4. The last class is that of metal cations which standard potential is below - 0.44 V ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ...). These cations may not directly affect the fixation by ZVI but compete with U(VI) for precipitation reactions for example, apart from modifying the ionic strength.

Note that, all these classes of materials interact with corrosion products and the blank surface of ZVI materials (sorption, complexation). Only materials from classes 1 and 2 will be investigated in the present study.

The variability of the groundwater composition has been documented<sup>12,13</sup> and the effects of groundwater constituents on the reactivity of both  $\text{Fe}^0$  materials<sup>14-16</sup> and corrosion products, at least for some contaminants<sup>11, 17</sup> have been investigated.

The influence of organic and inorganic ligands on U(VI) uptake by  $\text{Fe}^0$  has not been systematically studied. Consequently, this study aims at evaluating the effects of selected organic (EDTA, HS) and inorganic ( $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{2-}$ ,  $\text{SO}_4^{2-}$ ) ligands on U(VI) co-precipitation by ZVI. For this purpose, not shaken batch experiments were conducted with a constant amount of well-characterized ZVI materials (15 g/L) and calculated amounts of selected ligands to yield the wished final concentration (mostly 10 mM). Leaching experiments were conducted with sodium carbonate (100 mM). The initial uranium concentration was 20 mg/L (0.084 mM).

## **Experimental Section**

### ***Iron Materials***

Five iron materials were selected for this study:

- a) one scrap iron from a recycling company (Metallaufbereitung Zwickau) termed as “ZVI1”.
- b) four commercially available  $\text{Fe}^0$  materials for groundwater remediation termed as “ZVI2”, “ZVI3”, “ZVI4” and “ZVI5”. ZVI2 is Hartgußstrahlmittel from Würth, ZVI3 is Hartguß-

granulat from Hermens, ZVI4 is Graugußeisengranulat from G. Maier Metallpulver GmbH - Rheinfelden, and ZVI5 is Eisenschwamm from ISPAT GmbH, Hamburg - all in Germany. ZVI5 is a direct reduced iron; all other materials are cast irons of different geometrical shapes. Apart from ZVI5, the commercial iron materials were used as obtained. ZVI5 was broken to small pieces and sieved whereas ZVI1 was solely sieved. The experiments were then conducted with the particle sizes between 1.0 and 1.6 mm, mostly without any chemical pretreatment. Table 1 summarizes the elemental composition of these materials. The analyses were made by X-Ray fluorescence spectrometry. Because of the particularity of his manufacturing technology, the structure of ZVI5 is porous (direct reduced iron).

In some experiments, ZVI1 and ZVI2 were pre-treated with 0.25 M HCl for 14 hours to free the iron surface from corrosion products.

### ***Fixation Experiments and Analytical Method***

The experimental procedure for the fixation experiments, the desorption by 0.1M Na<sub>2</sub>CO<sub>3</sub> and the analytical method are described elsewhere<sup>8</sup> and will not be repeated here. In all experiments the background solution was the tap water (TW: reference system) of the city of Freiberg (Saxonia, Germany) of composition (mg/L) Cl<sup>-</sup>: 7.5, NO<sub>3</sub><sup>-</sup>: 17.5, SO<sub>4</sub><sup>2-</sup>: 42, Na<sup>+</sup>: 7.1, K<sup>+</sup>: 1.6, Mg<sup>2+</sup>: 6.8 and Ca<sup>2+</sup>: 37.1 (pH 7.2<sub>l</sub>).

All experiments were performed in triplicate. Error bars given in figures represent the standard deviation from the triplicate runs.

## **Results and Discussion**

The experiments were compared on basis of the total, the reversible and the irreversible fixation ( $P_{\text{tot}}$ ,  $P_{\text{rev}}$  and  $P_{\text{irrev}}$ ), defined by Eq. 1, 2 and 3:

$$P_{\text{tot}} = 100\% [1 - (C/C_0)] \quad (1)$$

$$P_{\text{rev.}} = 100\% [(C_0(V_0 - V_1) / V_0(C_0 - C))] \quad (2)$$

$$P_{\text{irrev.}} = 100\% [1 - (C/C_0) - (C_1V_0 - C_0V_1)/C_0V_0] \quad (3)$$

where  $C_0$  and  $C$  are the initial and the U concentration after the fixation experiment respectively.  $C_1$  is the U concentration after the desorption experiment with 100 mM  $\text{Na}_2\text{CO}_3$ .  $V_0$  gives the initial volume, and  $V_1$  the volume after removing about 13 mL of the solution for U analysis at the end of the fixation experiment.

For the comparison of the efficiency of ZVI materials for a process  $i$  in different systems, the relative U fixation ( $P_i^{\text{rel}}$ ) was defined by Eq. 4 as:

$$P_i^{\text{rel}} = 100\% [P_i/P_{i0}]$$

$P_i$  and  $P_{i0}$  been the fixation (total or irreversible) efficiency of a process in the system  $i$  relative to the reference system  $i_0$ .

### **Rationale for choice of the experimental conditions**

Ligands selected for this study are known for their interactions with ZVI, iron corrosion products or U(VI)<sup>12,14,18</sup>. A Humic substance (HS from Aldrich) and an EDTA (disodic salt from Merk) were used as proxies for organic ligands which occur frequently in soil and subsurface environments. On the other hand the tested inorganic ligands ( $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ) are ubiquitous in most subsurface environments or can occur in an iron reactive barrier (ref. 11 and references therein). Consequently, they may influence the U(VI) co-precipitation by ZVI via adsorption and complexation with the surface sites of ZVI and its corrosion products. Elevated ligands concentrations were used to intensify the expected interactions with ZVI, U(VI) and corrosion products. Apart from  $\text{CO}_3^{2-}$ , 100 mM of the inorganic ligands were used. The used concentration of humic substance was 80 mg/L.

To avoid high dissolved iron concentrations that are known to disturb U analysis by the used ArsenazoIII-method (ref. 19 and references therein) a preliminary work was conducted to determine the operative EDTA concentration. Figure 1a shows that for EDTA concentrations below 14 mM, the Fe concentration was about 100 mg/L. Properly calibrated Fe(III)-U(VI) solutions enabled the minimisation of the impact of Fe(III) on U analysis.<sup>18</sup> An EDTA concentration of 12.5 mM was selected for this study.

For carbonates ions, a similar experiment as for EDTA was conducted and the results on Fig 1b show that, for  $\text{CO}_3^{2-}$  concentration  $> 25$  mM the U uptake significantly decreases. This is justified by the known affinity of U(VI) for  $\text{CO}_3^{2-}$  ions.<sup>12</sup> However this uptake decrease was not monotone (Fig 1b). The non monotone U(VI) removal decrease with increasing  $\text{CO}_3^{2-}$  concentration was reproducible but not further investigated. It should be pointed out that, even at 50 mM  $\text{CO}_3^{2-}$  (removal minimum), U(VI) removal (about 35%) was still higher than at 6 mM EDTA (about 22 %). This result shows clearly that, in the presence of  $\text{Na}_2\text{CO}_3$ , at concentrations as higher as 100 mM, U(VI) removal still occur. This can be the result of both U(VI) fixation onto newly formed iron carbonate species<sup>20,21</sup> or U(VI) precipitation e.g. as uranates,  $\text{Na}_2\text{UO}_4$ .<sup>22</sup> In all the cases U(VI) removal is almost irreversible (Fig. 1b).

This result is interesting because 0.1 M  $\text{Na}_2\text{CO}_3$  (100 mM) is usually used in the literature as U(VI) desorbing agent. To test the reproducibility of this experiment, two sets of experiments were conducted for duration up to 75 days with 50 mM  $\text{CO}_3^{2-}$ . The results in Tab. 2 show that the uptake was almost irreversible, the desorption experiments been achieved with 100 mM  $\text{Na}_2\text{CO}_3$ . In fact the reversible fixation efficiency varies between 1.0 and 6.2 % under the experimental conditions.

Considering the particular fact that the irreversibility of U(VI) onto carbonate species has been documented,<sup>20</sup>  $\text{Na}_2\text{CO}_3$  should have not been used in testing ZVI materials for U(VI) remediation. Noubactep et al.<sup>22</sup> have proposed the use of natural  $\text{CO}_2$ -saturated mineral waters, which provide sufficient amounts of  $\text{HCO}_3^-$  for U(VI) complexation at neutral near pH values.

### **Effects of selected ligands**

Figure 2 shows the results of the total, reversible (2a) and irreversible (2b) U(VI) fixation by ZVI1 (scrap iron) for 14 days in the presence of 12.5 mM EDTA, 50 mM  $\text{CO}_3^{2-}$ , 10 mM of  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ , and 80 mg/L HS. This equilibration time was chosen to enable a differentiation of the impact of the ligands on the U(VI) fixation efficiency under the

experimental conditions based on preliminary experiments.<sup>18</sup> The reference system was the experiment in the tap water (TW).

From Fig. 2a, it can be seen that the total fixation's efficiency diminished as response of the systems to the addition of all ligands, except  $\text{PO}_4^{3-}$ . The total fixation efficiency varies from 23 % for EDTA to 99 % for  $\text{PO}_4^{3-}$ , the increasing order of efficiency been:

$$\text{EDTA} < \text{CO}_3^{2-} < \text{SO}_4^{2-} < \text{NO}_3^- < \text{NO}_2^- < \text{Cl}^- < \text{HS} < \text{TW} < \text{PO}_4^{3-}$$

Figure 2a also shows the variation of the reversible fixations. From Fig. 2a, it can be seen that for EDTA and  $\text{CO}_3^{2-}$  the uptake was practically irreversible, whereas the extent of the reversibility for other ligands were very different, varying from 12 % for  $\text{SO}_4^{2-}$  to 47 % for  $\text{NO}_2^-$ . Note that the reversible fixation ( $P_{\text{rev}}$ ) is relative to the mass of fixed uranium (total fixation), whereas  $P_{\text{tot}}$  and  $P_{\text{irrev}}$  are relative to the initial mass of U.

After the recovery experiment with 100 mM  $\text{Na}_2\text{CO}_3$ , the irreversible fixation efficiency varies from 23 % for EDTA to 73 % for TW (Fig. 2b), the increasing order of efficiency been:

$$\text{EDTA} < \text{NO}_2^- < \text{CO}_3^{2-} < \text{SO}_4^{2-} < \text{Cl}^- < \text{NO}_3^- < \text{PO}_4^{3-} < \text{HS} < \text{TW}.$$

When comparing the order of efficiency in the total and irreversible fixation for different ligands, it becomes clear that the extend to which corrosion products influence the U(VI) uptake for individual ligands is quite complicated.

$\text{PO}_4^{3-}$  has as a competitive complexant for U(VI) a particular position.<sup>12</sup> The observed total fixation is the result for U(VI) precipitation with  $\text{PO}_4^{3-}$ , U(VI) co-precipitation with in situ generated corrosion products, sorption onto aged corrosion products and surface of the  $\text{Fe}^0$  material. U(VI) precipitation with  $\text{PO}_4^{3-}$  and U(VI) co-precipitation with in situ generated corrosion products are almost irreversible under the experimental conditions.<sup>18</sup>

EDTA exhibits the lowest fixation efficiency, it can be assumed, that the fixed U(VI) amount (23 %) is the sufficient amount to build a U(VI) multi-layer at the available surface of the ZVI material (15 g/L). Qui et al.<sup>23</sup> reported that these U(VI) layers do not prevent iron to corrode.

This statement is confirmed by the results on Fig. 1a. U(VI) removal remains practically constant when the iron concentration varies from 45 to more than 700 mg/L.

Humic substances usually form complexes with U(VI),<sup>24,25</sup> whose affinity for corrosion products is documented.<sup>26</sup> The U(VI) analysis after the addition of 100 mM Na<sub>2</sub>CO<sub>3</sub> was disturbed by a dark coloration such that the obtained results for  $P_{rev}$  and  $P_{irrev}$  only have indicative functions.

To further investigate the nature of the interactions in the system “ZVI-corrosion product-U(VI)-ligands” and the impact on the removal mechanism, the experiments with HS, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> EDTA and CO<sub>3</sub><sup>2-</sup> were repeated for scrap iron (ZVI1) and four commercial Fe<sup>0</sup> materials.

### **Effects of selected ligands on various ZVI**

Table 3 summarises the results of U(VI) total fixation by the scrap iron (ZVI1) and four commercial ZVI materials (ZVI2, ZVI3, ZVI4 and ZVI5) in the presence of EDTA, HS, CO<sub>3</sub><sup>2-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and NO<sub>3</sub><sup>-</sup>. The reference system is the system in tap water (TW).

Once again, the decrease of  $P_{tot}$  was the standard response of the systems to the addition of the ligands. The materials in Tab. 3 are listed from the top to the bottom in the order of increasing  $P_{tot}$  in tap water; that is: ZVI2 < ZVI3 < ZVI4 < ZVI1 < ZVI5. The same efficiency order is obtained in the systems with HS, NO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>. Each of the other systems exhibits a different behaviour. The most important consequence of these results is that, several materials should be tested for their reactivity under particular site specific conditions of an application and the best should be retained. For example if a specific groundwater has a composition similar to that of the used tap water (TW) or is rich in organic matter, NO<sub>3</sub><sup>-</sup> or CO<sub>3</sub><sup>2-</sup>, then ZVI5 is the more reactive material to be considered. If on the contrary the groundwater is rich in chloride (Cl<sup>-</sup>) then ZVI4 will be the most indicated. On the other hand, if the EDTA concentration of a groundwater containing U(VI) is high, alternative remediation technologies have to be found.



The current material selection strategy is not appropriate to address long term reactivity of ZVI material. Therefore it is possible, that a material as reactive as porous ZVI5 loss its reactivity after few months. For reactive barriers however, materials are supposed to give satisfactorily remediation goal for several decades.<sup>27</sup>

### **Effects of ZVI pre-treatment**

In order to further investigate the reactivity of ZVI materials for U(VI) uptake under subsurface conditions, two sets of U(VI) fixation experiments were conducted with 15 g/L ZVI1 and 25 g/L ZVI2 and four ligands ( $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ , EDTA and HS). While not pre-treated ZVI2 was of smooth surface being almost completely covered with a continuous oxide layer, ZVI1 has a rough surface that prevents the formation of such an oxide layer at its surface.

The first set of experiment was identical to the above described experiment and the second set consisted in pre-washing both  $\text{Fe}^0$  materials for 14 hours with a 0.25 M HCl solution. This pre-treatment aimed at favoring a slow and progressive dissolution of the oxides on ZVI without strongly affecting the surface structure of the material.<sup>28</sup> At the end of this washing time the surface was optically clean (metallic glaze). It is possible that not all the oxide on the surface of the materials was removed in this manner. However, it was not the intention of this study to work with totally clean  $\text{Fe}^0$  material, but rather to evaluate the effect of the presence of atmospheric corrosion products.

The results for ZVI1 in Tab. 4 can be summarized as follows:

- With untreated materials, U(VI) total fixation is slightly accelerated in the system with  $\text{Cl}^-$  ( $P_{\text{tot}}^{\text{rel}} = 104 \%$ ). In all other systems the total fixation decreases, the relative fixation been 88, 69 and 19 % for the systems with HS,  $\text{CO}_3^{2-}$  and HS respectively.
- The acidic pre-treatment of ZVI1 induces an increase of the absolute value of  $P_{\text{tot}}$  in all system, except in the system with 50 mM  $\text{CO}_3^{2-}$ , where  $P_{\text{tot}}$  decreases from 62 to 48 %. This results suggests that even in the presence of elevated concentrations of carbonate ions, U(VI) sorbs onto iron oxides.

- The comparison of the  $P^{rel}$  ( $P^{rel}_{tot}$  and  $P^{rel}_{irrev}$ ) values from the two sets of experiments shows that the pre-treatment enhances the U(VI) immobilization efficiency of the material except in the presence of  $CO_3^{2-}$ . This is due to the fact that, when U(VI) is sorbed onto aged iron oxides (initially present at the surface), it is readily desorbed in 100 mM  $Na_2CO_3$ . In the experiment with pre-treated ZVI, U(VI) is progressively sorbed onto in situ generated corrosion product and is entrapped in their mass as they aged (coprecipitation) and is therefore not available for desorption with  $Na_2CO_3$ .<sup>8</sup> When ZVI is freed from corrosion product, only the blank surface of ZVI with smaller affinity to U(VI) is available for sorption.<sup>18</sup> Therefore it is not surprising that pre-washing diminish the uptake in the presence of carbonate ions.

The results of the experiment with ZVI2 (Tab. 4) show the same trend as with ZVI1 with the particularity that the effect of the pre-treatment was more pronounced, yielding to  $P^{rel}_{irrev}$  values of more than 170 %. Furthermore pre-washing decreases U(VI) removal in the presence of humic substances. U(VI) removal in the presence of EDTA was not influenced by the acidic treatment. This result supports the fact that ZVI2 was almost completely covered with an oxide layer. This oxide layer interacts with HS or dissolves in EDTA. Note that if U(VI) removal was the result of a “reductive precipitation”, freeing the iron surface from corrosion products would have increase the uptake efficiency.

This result suggests that for a carbonate rich groundwater ZVI2 (or generally smooth ZVI) is not indicated. As discussed above groundwater with elevated concentration of EDTA should not be treated with ZVI reactive barrier. Humic substances will slightly lower the efficiency of reactive barriers for U(VI) remediation whereas  $Cl^-$  practically has a rather positive effect on the remediation. This chloride enhancing iron corrosion properties is known and documented.<sup>14,29,30</sup> In fact, chloride ions participate directly in anodic dissolution reactions of metals ; thus their presence tends to increase iron corrosion.

## **Implications for U(VI) removal barriers**

The results of this study show that EDTA and carbonate ions sensibly affect the efficiency of U(VI) co-precipitation by ZVI. It is suggested that alternative to ZVI should be found when elevated EDTA concentration are present (or expected). For carbonate rich groundwater a rational choice of material can enable satisfactorily mitigation effect. However, the long term behaviour of such materials is yet to be addressed.

From the other tested ligands ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{Cl}^-$ ,  $\text{HS}^-$ ,  $\text{PO}_4^{3-}$ ) only chloride shown an enhancing impact on the co-precipitation by ZVI. However, even at a chloride rich site, not the most reactive materials (ZVI1 or ZVI5 in this study) will be selected for application, but rather materials, that are capable of assuring satisfactorily remediation goal for several decades. It should be kept in mind, that enhanced corrosion yields to more corrosion products (which volume are at least 2.3 times larger than that of Fe atom in the ZVI material) that limit the volume of pore spaces in the reactive barrier beside potentially inhibiting the electrochemical dissolution of ZVI.

U(VI) co-precipitation in ZVI reactive barrier is based on the continuously production of fresh and very reactive corrosion products that incorporate U(VI) into their structure while aging.<sup>7</sup> At any specific site, several materials are to be properly tested for their long term efficiency at removing the target contaminant. This study shows that a direct reduced iron (ZVI5) is capable of efficiently remove U(VI) from aqueous solution in the presence of various ligands. The long term reactivity of the material is yet to be investigated. For the long term immobilization of U(VI) by ZVI, it is important that fresh iron oxide is present in the barrier zone when the contaminant is transported into the barrier. In nature the long term iron corrosion can be influenced by availability and activity of microorganisms and/or their metabolites<sup>10</sup>. Therefore, as more as possible, the possible effect of indigenous microorganisms at specific site are to be considered.

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**Table 1.** Elemental composition of iron materials used in this study.

	elemental composition (%)								
	C	Si	Mn	P	S	Cr	Mo	Ni	Fe
<b>ZVI1</b>	3.52	2.12	0.93	n.d.	n.d.	0.66	n.d.	n.d.	n.d.
<b>ZVI2</b>	3.39	0.41	1.10	n.d.	0.105	0.34	n.d.	0.088	n.d.
<b>ZVI3</b>	3.13	0.17	0.42	0.053	0.065	0.16	n.d.	0.23	n.d.
<b>ZVI4</b>	3.13	2.17	0.36	0.022	0.029	0.077	n.d.	0.056	n.d.
<b>ZVI5</b>	1.96	0.12	0.09	0.027	0.14	0.003	n.d.	<0.001	n.d.

(\*) n.d. = not determined and

**Tabelle 2:** Variation of total and reversible fixation of U(VI) by the scrap iron (ZVI1) in the presence of 0.05 M Na<sub>2</sub>CO<sub>3</sub>. Two non parallel experiments were conducted (t values). The experiments were conducted in triplicate, s<sub>i</sub> represents the standard deviation for each triplicate.

<b>t</b>	<b>P<sub>tot</sub></b>	<b>S<sub>tot</sub></b>	<b>P<sub>rev</sub></b>	<b>S<sub>rev</sub></b>	<b>t</b>	<b>P<sub>tot</sub></b>	<b>S<sub>tot</sub></b>	<b>P<sub>rev</sub></b>	<b>S<sub>rev</sub></b>
<b>[days]</b>	<b>[%]</b>	<b>[%]</b>	<b>[%]</b>	<b>[%]</b>	<b>[days]</b>	<b>[%]</b>	<b>[%]</b>	<b>[%]</b>	<b>[%]</b>
<b>7</b>	84.8	6.2	4.0	2.1	<b>10</b>	79.3	3.2	1.0	0.5
<b>14</b>	92.0	3.0	7.1	3.6	<b>17</b>	84.4	1.7	1.3	0.9
<b>21</b>	92.5	3.6	6.1	1.0	<b>24</b>	88.7	3.0	1.3	0.4
<b>28</b>	93.7	3.1	6.7	2.0	<b>34</b>	93.4	2.5	0.8	0.7
<b>35</b>	97.4	0.2	4.1	1.1	<b>44</b>	94.4	3.1	1.0	0.7
<b>42</b>	95.7	1.8	5.8	1.8	<b>54</b>	97.6	0.7	1.9	0.7
<b>48</b>	93.3	2.8	7.2	2.1	<b>64</b>	97.1	0.3	1.9	0.7
<b>56</b>	95.3	2.2	5.6	1.4	<b>74</b>	97.0	0.1	2.3	0.4



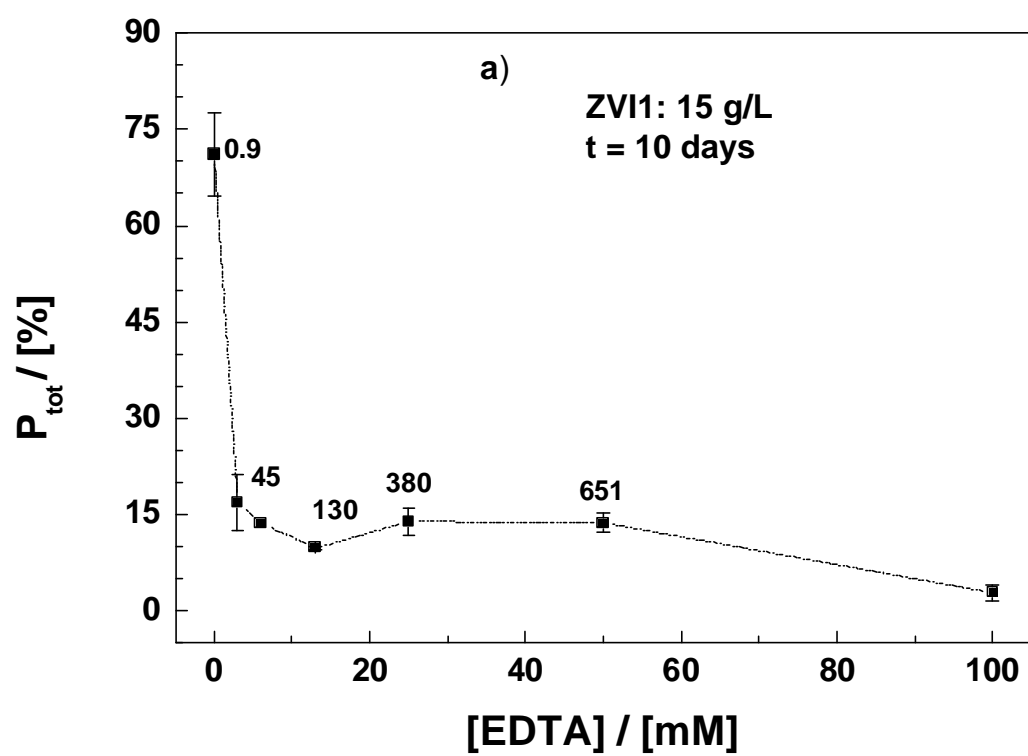
**Table 3:** Variation of total fixation of U(VI) for the five ZVI materials in the presence of different ligands. TW = tap water is the reference system, HS = humic substance.

<b>ZVI</b>	<b>total fixation (%)</b>						
	<b>TW</b>	<b>HS</b>	<b>Cl<sup>-</sup></b>	<b>SO<sub>4</sub><sup>2-</sup></b>	<b>NO<sub>3</sub><sup>-</sup></b>	<b>EDTA</b>	<b>CO<sub>3</sub><sup>2-</sup></b>
<b>ZVI2</b>	81	66	57	43	34	19	0
<b>ZVI3</b>	82	76	55	49	45	10	7
<b>ZVI4</b>	91	84	77	54	65	22	6
<b>ZVI1</b>	95	90	66	71	64	8	26
<b>ZVI5</b>	96	91	71	64	76	26	69

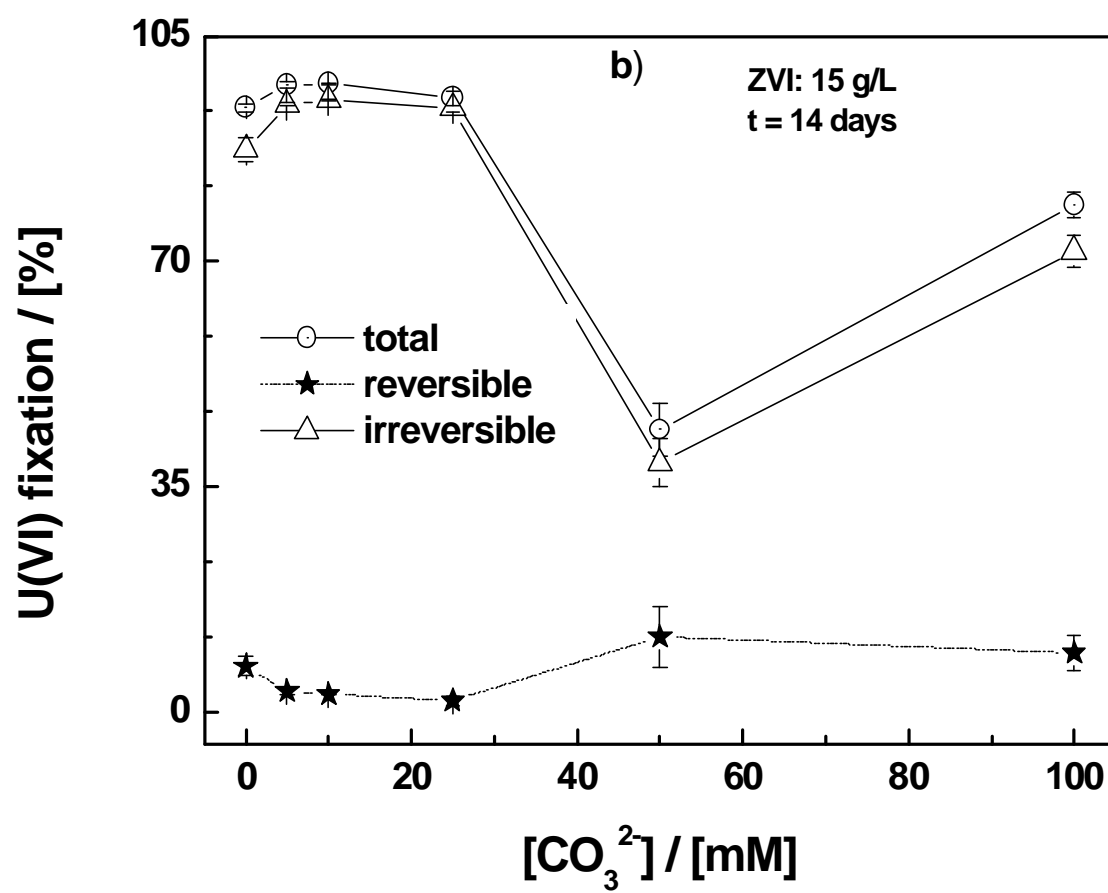
**Table 4:** Variation of the relative total and irreversible fixation of U(VI) for untreated and 0.25 M HCl washed ZVI1 and ZVI2 in the presence of selected ligands. The reference for the definition of  $P^{rel}$  is the removal efficiency for untreated ZVI1 in tap water (TW). HS = humic substance. The brackets symbolise the coverage of the surface with corrosion products (untreated ZVI).

Milieu	ZVI1 (scrap iron)				ZVI2 (commercial iron)			
	$P_{tot}$	$P_{irrev}$ (%)	$P_{tot}^{rel}$	$P_{irrev}^{rel}$	$P_{tot}$	$P_{irrev}$ (%)	$P_{tot}^{rel}$	$P_{irrev}^{rel}$
	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]
[TW]	90	64	100	100	65	33	100	100
[HS]	79	71	88	111	48	37	74	114
[Cl]	94	62	105	98	63	29	96	89
[EDTA]	17	17	19	27	9	9	14	28
[CO <sub>3</sub> <sup>2-</sup> ]	62	62	69	97	54	54	82	164
TW	93	73	103	115	73	57	113	173
HS	81	77	90	121	38	29	58	88
Cl	90	71	100	112	38	33	58	99
EDTA	22	22	24	34	10	10	16	32
CO <sub>3</sub> <sup>2-</sup>	48	48	54	75	48	45	74	136

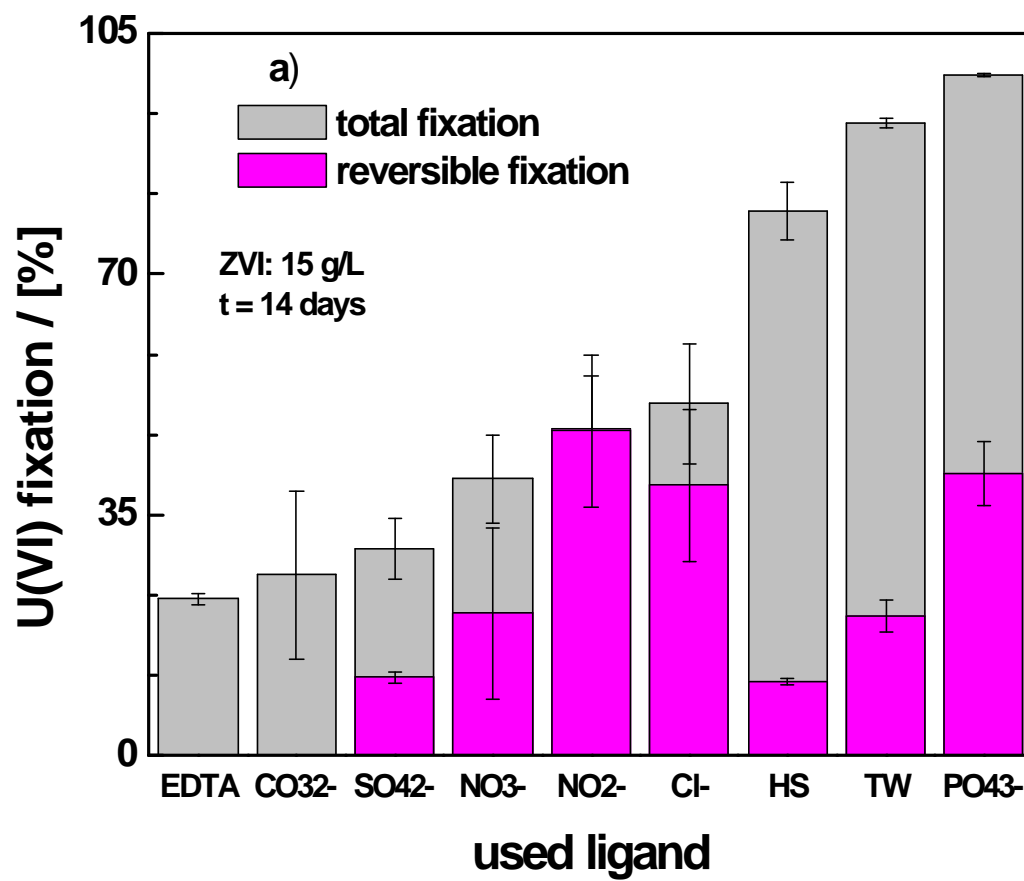
Noubactep Fig. 1a:



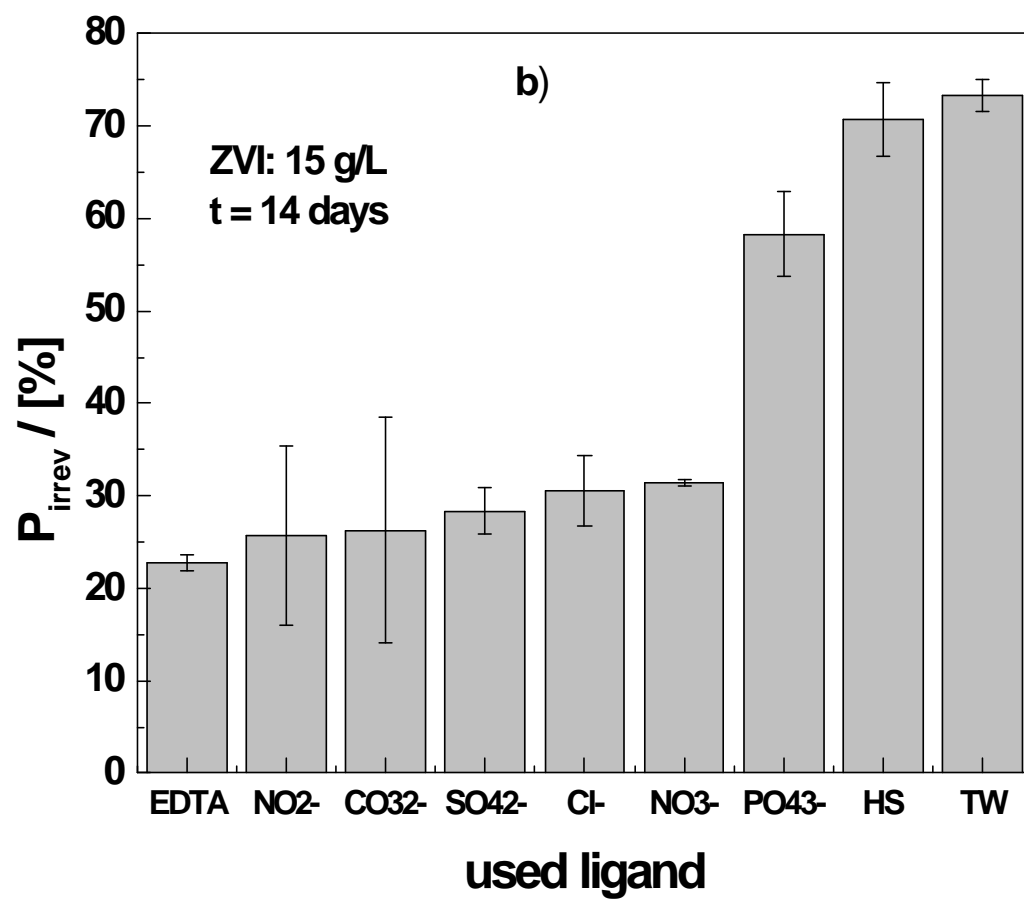
Noubactep Fig. 1b:



Noubactep Fig. 2a:



Noubactep Fig. 2b:



## Figure captions

**Figure 1:** Variation of the U(VI) fixation from the aqueous solution by ZVI 1 (scrap iron) as function of (a) the EDTA and the carbonate (b) concentrations. All experiments have been done in triplicate. Error bars give standard deviations. The represented lines are not fitting functions, they just joint the points to facilitate visualization. The values on the curve (a) are the iron concentrations in mg/L.

**Figure 2:** Uranium (VI) uptake by ZVI 1 (scrap iron) in 12.5 mM EDTA, 50 mM  $\text{CO}_3^{2-}$ , 80 mg/L humic substance (HS) and 10 mM of  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ . The reference system is the experience in tap water (TW). (a) total and reversible fixation, (b) irreversible fixation. The desorption experiments were conducted with 100 mM  $\text{Na}_2\text{CO}_3$ . All experiments have been done in triplicate. Error bars give standard deviations.